

ALTERATION OF THE FREE SURFACE ENERGY OF
SOLIDS

1. EFFECT OF HEAT TREATMENT OF METALS IN AIR
2. EFFECT OF HEAT TREATMENT OF METALS IN A VACUUM AND IN
SEVERAL GASES

BY
MIKE A. MILLER

A DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. II

EFFECT OF HEAT TREATMENT OF METALS IN AIR

It was shown in a previous paper (2) that the vertical-rod method can be used for the measurement of solid-liquid-air and solid-liquid-liquid contact angles and that it is particularly suitable for obtaining information concerning changes in free surface energy of metals and of other solids which can be obtained in the form of rods. In the present investigation the effect of heat treatment in air on gold, platinum, and steel was studied by means of the vertical-rod method. The liquids used were water, benzene, α -bromonaphthalene, and acetylene tetrabromide, purified according to methods presented in earlier papers from this laboratory.

PREPARATION OF A STANDARD SURFACE

In order to measure the change in the angle of contact formed by a liquid on a metal after heat treatment of the metal, it was necessary that the initial surface condition of the metal be definite and reproducible. A method of pretreatment of gold and platinum was found which gave a standard surface whose solid-water-air contact angle could be reproduced to within $\pm 4^\circ$. The gold or platinum rod was first carefully and completely scraped with the edge of a carborundum crystal, was next polished with the edge of a roughly ground glass plate, and was then polished with a finely ground glass plate until the surface, as observed under a microscope, was practically free of microscopic striations. The rod was handled at all times with clean tin foil. After polishing, it was washed briefly in concentrated hydrochloric acid, then thoroughly with distilled water. It was then steamed for one hour and finally heated at 100°C . in an electric oven in air for one hour. The standard surface gold-water-air contact angle was $68^\circ \pm 4^\circ$. The standard surface platinum-water-air contact angle was $63^\circ \pm 4^\circ$. Only rods giving values within these limits were used for subsequent heat treatment.

Steel, owing to its greater susceptibility to oxidation, did not give a "standard" surface after the same pretreatment as that given to gold and platinum. Various attempts to obtain a standard steel surface were

made, but no satisfactory method of treating steel in air was found. Measurements on heat-treated steel were made, but since no satisfactory reference value was found, data on steel will not be given in this paper.

The thorough polishing given the metals in the pretreatment tends to make the surface entirely amorphous (4). This polishing removes the effects of previous heat treatments so far as the surface is concerned, for, though evidence obtained from the literature (5, 6), as well as from our own experiments, indicates that heat treatment may produce certain specific

TABLE 1

Equilibrium advancing contact angles and adhesion tension values for water on heat-treated gold and platinum

HEAT TREATED FOR 1 HOUR AT	ADVANCING CONTACT ANGLES AND ADHESION TENSION VALUES					
	Gold			Platinum		
	θ_{12}	$\cos \theta_{12}$	A_{12}	θ_{12}	$\cos \theta_{12}$	A_{12}
°C.						
100	68°	0.3746	26.97	63°	0.4540	32.69
200	57°	0.5446	39.21	49°	0.6561	47.24
300	45°	0.7071	50.91	36°	0.8090	58.25
400	36°	0.8090	58.25	25°	0.9063	65.25
500	25°	0.9063	65.25	13°	0.9744	70.16
600	13°	0.9744	70.16	0°		

TABLE 2

Alteration with time of standing in air of equilibrium advancing contact angles and adhesion tension values for water on heat-treated gold

HOURS IN AIR	GOLD PREVIOUSLY HEAT- TREATED AT 100°C. FOR 1 HOUR			GOLD PREVIOUSLY HEAT- TREATED AT 400°C. FOR 1 HOUR			GOLD PREVIOUSLY HEAT- TREATED AT 600°C. FOR 1 HOUR		
	θ_{12}	$\cos \theta_{12}$	A_{12}	θ_{12}	$\cos \theta_{12}$	A_{12}	θ_{12}	$\cos \theta_{12}$	A_{12}
$\frac{1}{4}$	68°	0.375	26.97	36°	0.809	58.25	13°	0.974	70.06
1	69°	0.358	25.81	39°	0.777	55.95	22°	0.927	66.76
5	70°	0.342	24.62	48°	0.669	48.18	38°	0.788	56.74
10	68°	0.375	26.97	50°	0.643	46.28	47°	0.682	49.10
24	71°	0.326	23.44	51°	0.629	45.31	53°	0.602	43.33
120	70°	0.342	24.62	57°	0.545	39.21	55°	0.574	41.30

internal effects as well as surface effects, the surface appears to be affected by internal conditions only if the rod is not sufficiently polished or if it is allowed to stand too long a time before being used after polishing.

CONTACT ANGLE MEASUREMENTS ON HEAT-TREATED GOLD AND PLATINUM IN AIR

The metal rods were first treated so as to obtain the standard surface. They were then heated for one hour at a definite temperature, the tem-

peratures for the different rods ranging in 100°C. steps from 100° to 600°C. $\pm 5^\circ$. The contact angle was measured not later than fifteen minutes after the rod had cooled to room temperature, this length of time being necessary to set up the rod system and to obtain proper focusing of microscope and camera. Measurements were carried out at a temperature of 25°C. $\pm 2^\circ$. The contact angle was photographed and its image was measured directly on the plate or was projected on a screen and measured (2). Table 1 gives the water-air advancing contact angles obtained with heat-treated gold and platinum, and the adhesion tension values, A_{13} , calculated from the cosines of these angles. It will be noted that the angle of contact decreases with progressively higher temperature of heat treatment.

TABLE 3

Interfacial contact angles, metal-water-organic liquid, for heat-treated gold and platinum

HEATED AT °C. FOR 1 HOUR	BENZENE			α -BROMONAPHTHALENE			ACETYLENE TETRABROMIDE		
	θ_{n3}	$\cos \theta_{n3}$	A_{1n}	θ_{n3}	$\cos \theta_{n3}$	A_{1n}	θ_{n3}	$\cos \theta_{n3}$	A_{1n}
Gold									
300	141°	-0.7771	77.88	146°	-0.8290	85.40	138°	-0.7431	79.37
400	113°	-0.3907	71.81	111°	-0.3584	73.16	115°	-0.4226	74.44
500	89°	+0.0175	64.65	86°	+0.0698	62.35	88°	+0.0349	62.88
600	78°	+0.2079	62.95	74°	+0.2756	58.69	83°	+0.1219	65.49
Platinum									
300	123°	-0.5446	77.15	123°	-0.5446	80.91	128°	-0.6157	81.83
400	85°	+0.0872	62.22	83°	+0.1219	60.28	86°	+0.0698	62.58
500	72°	+0.3090	59.44	77°	+0.2250	60.80	75°	+0.2588	60.25
600	61°	+0.4848	(55.18)*	63°	+0.4540	(53.11)*	65°	+0.4226	(55.81)*

* All the A_{1n} values except those marked ()* were calculated from the equation $A_{13} - A_{1n} = S_{n3} \cos \theta_{n3}$ (see reference 3) using the data from tables 1 and 3. The three A_{1n} values marked ()* were calculated from the empirical equation $A_{1n} = (12.8 - S_{n3}) \cos \theta_{n3} + 65.2$ (see reference 1).

When the heat-treated metals stood in air, the contact angle assumed a larger value (2, 7). The rate and magnitude of this change for gold are shown in table 2. Similar data were obtained with platinum. It will be noted that the initial change was very rapid. Such age-change phenomena were probably due to sorption.

WATER-ORGANIC LIQUID INTERFACIAL CONTACT ANGLE MEASUREMENTS ON GOLD AND PLATINUM

Gold and platinum rods were treated to obtain the standard surface, and the interfacial contact angle, metal-water-organic liquid, was measured.

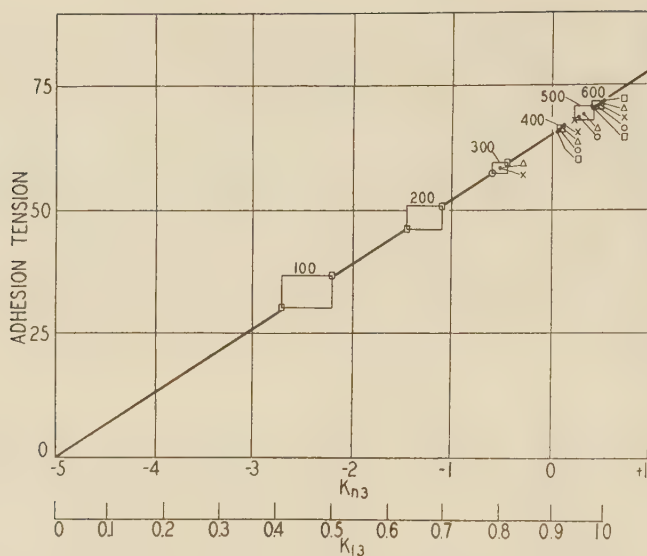


FIG. 1. Change in adhesion tension with heat treatment. Platinum one-quarter of an hour in air. $\square$, platinum-water-air; $\triangle$, platinum-benzene-water; $\circ$, platinum-acetylene tetrabromide-water; $\times$, platinum- α -bromonaphthalene-water.

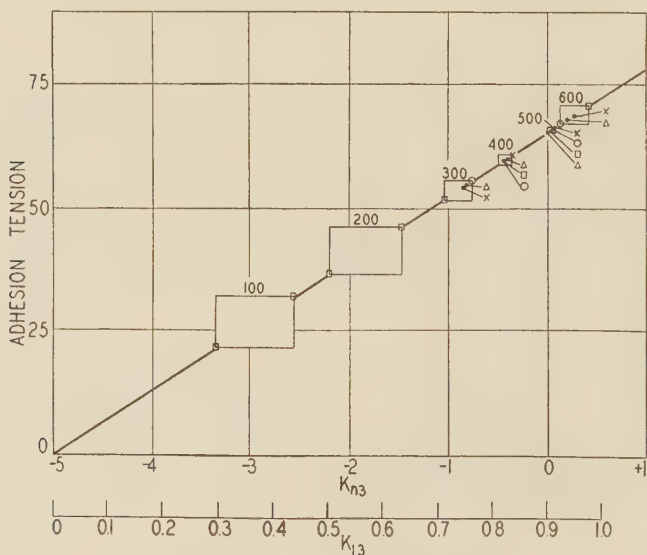


FIG. 2. Change in adhesion tension with heat treatment. Gold one-quarter of an hour in air. $\square$, gold-water-air; $\triangle$, gold-benzene-water; $\circ$, gold-acetylene tetrabromide-water; $\times$, gold- α -bromonaphthalene-water.

The results are presented in table 3. All angles were measured through the water phase. As in the case of the metal-water-air angles, the metal-water-organic liquid angles decreased with increasingly higher temperature of heat treatment. For the three systems of liquids investigated, the interfacial contact angles were approximately the same against a given solid surface, the deviation in most cases being well within the limits prescribed for the standard surface (i.e., $\pm 4^\circ$ for the metal-water-air contact angle).

Since the interfacial angles formed on these metals by the three organic liquids were all practically the same, the empirical equations developed by Bartell and Bartell (1), relating the cosine of the interfacial angle ($\cos \theta_{n3}$)¹

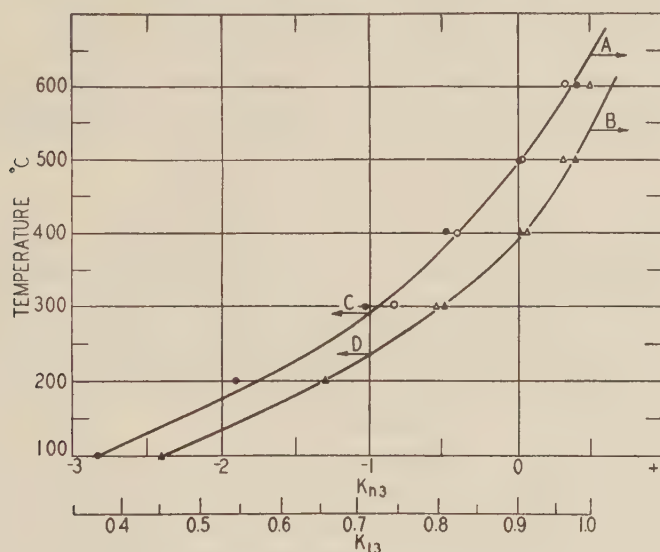


FIG. 3. Change of cosine of contact angle K_{n3} and K_{13} with heat treatment. ●, gold-water-air; ▲, platinum-water-air; ○, organic liquid-water-gold; △, organic liquid-water-platinum.

to adhesion tension, may apply to these metals. That they do apply can readily be shown.

If adhesion tension values, calculated from the observed advancing water-air contact angles on metals after various heat treatments, are plotted against K_{13} , and if the corresponding K_{n3} values for the given heat-

¹The symbols used in this paper are the same as those used in recent papers from this laboratory, i.e., S represents surface tension, interfacial tension, or free surface energy, A represents adhesion tension, θ the contact angle, and K is the same as the cosine of θ within the limits of $+1$ and -1 , but may take on values greater than $+1$ and less than -1 . The subscripts 1, n , and 3 refer to the solid, any organic liquid, and water, respectively.

treated metals are plotted as a second abscissa scale, the graphs shown in figures 1 and 2 are obtained. The straight line drawn through these points is the so-called "water-line" (1) whose equation is:

$$A_{13} = 12.8K_{n3} + 65.2$$

The area enclosed in the rectangles represents the limits of experimental error for the given temperatures of pretreatment.

If temperature of heat treatment is plotted against K_{13} and against K_{n3} , smooth curves, as shown in figure 3, are obtained. From inspection of these curves it can be seen that gold and platinum, heat-treated at the temperatures corresponding to the ordinates of points *A* and *B*, respectively, should exhibit zero advancing water-air contact angles. Gold and platinum, heat-treated at temperatures corresponding to the ordinates of points *C* and *D*, respectively, should exhibit water-organic liquid interfacial contact angles equal to 180°. This was found experimentally to be correct.

SUMMARY

Rods of gold and platinum were given a special pretreatment so as to have standard surfaces for reference. Such a standard surface could not be produced on rods of steel treated in air. Standard surface rods of gold and platinum were subjected to heat treatment in air at given temperatures ranging between 100° and 600°C., and changes, due to heat treatment, in contact and interfacial contact angles were measured by the vertical-rod method.

With low-temperature treatment the metals were fairly strongly organophilic, while with higher temperature treatments they were less strongly organophilic and could even be caused to become hydrophilic in nature. The changes were probably due to oxidation and recrystallization. The surface properties were found to alter with time of standing after heat treatment.

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ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. III

EFFECT OF HEAT TREATMENT OF METALS IN A VACUUM AND IN SEVERAL GASES

Recent communications from this laboratory (2, 3) have shown that large changes in surface properties of metals, caused by heat treatment of the metals in air; can be measured by measurement of the metal-water-air and metal-water-organic liquid contact angles. A method of pretreatment of metals to obtain a standard reference surface has been described (3). This method included polishing and mild heat treatment, both operations being carried out in air.

The present investigation had as its major aim the evaluation of the specific effects of the gas phase during heat treatment of metals. For this investigation a somewhat different method of preparation of standard metal surface was used, since metals polished in air undergo wear oxidation (5, 8) as well as grain or crystal fragmentation (6). Even noble metals such as gold are known to undergo wear oxidation (5) and to be capable of existing in several distinct oxidation patterns (7). For the present investigation standard metal surfaces were prepared by thorough polishing of the metals in an atmosphere of nitrogen and subsequent mild heat treatment in a vacuum. Differences of surface due to different degrees of crystal fragmentation were eliminated by the thorough polishing (4); and the use of a nitrogen atmosphere during polishing and of a vacuum (evacuated from a nitrogen atmosphere) during heat treatment, removed almost entirely the possibility of wear oxidation or heat oxidation.

The experiments on heat treatment of standardized metal surfaces fell naturally into two groups: (a) heat treatment of metals in a vacuum and (b) heat treatment of metals in different gases. In the experiments in a vacuum, gold, platinum, copper, and 18-8 stainless steel were used. In the experiments in gases, silver, aluminum, tungsten, and brass were used in addition to the metals listed above. The gases used were nitrogen, hydrogen, and oxygen. The nitrogen was purified by passing tank nitrogen successively through copper-ammonium carbonate solution, molten phosphorus, a reduced-copper furnace, and suitable drying towers. Oxygen

and hydrogen were carefully dried before being used. The liquids used for contact angle measurements were water, benzene, α -bromonaphthalene, and acetylene tetrabromide, all carefully purified.

PRODUCTION OF STANDARD METAL SURFACES AND MANIPULATION OF THE
VACUUM APPARATUS FOR SOLID-LIQUID-GAS CONTACT ANGLE
MEASUREMENTS

For production of a standard metal surface, the metal rod was drastically polished in air, being handled with clean tin foil at all times. First, it was thoroughly scraped with the edge of a carborundum crystal, then it was polished with the flattened finely ground end of a quartz rod. The metal

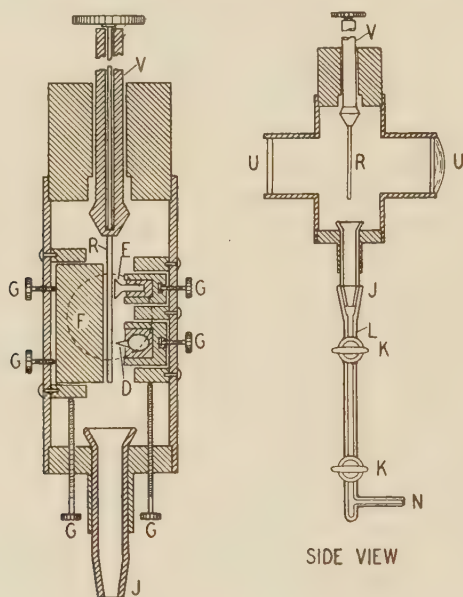


FIG. 1. Polishing apparatus

rod was then placed in the holder, V, figure 1, of the polishing apparatus and nitrogen was allowed to flow through this apparatus for at least one hour. After this the rod was polished in a nitrogen atmosphere in the same way as it had been polished in air, by means of the carborundum crystal, D, and the quartz rod, E. When a surface had been obtained which was practically free of microscopic striations, as shown by examination through the magnifying window, U, of the apparatus, the rod was released from its holder into the lower glass compartment, L, shown in figure 1, side view. In this compartment it was transferred in an atmosphere of nitrogen to the main vacuum apparatus, figure 2.

The vacuum apparatus had previously been swept out with pure nitrogen

for at least one hour by means of a nitrogen line connected at B. With the gas flowing through the apparatus, the heating unit (carrying W, the heating coil) was placed in position. The apparatus was flushed out with nitrogen for another hour after the rod and heating unit were in place. The gas line was then disconnected; stopcock (mercury-seal type) S was closed, and a mercury-seal cap placed over the lower opening, B. The entire unit was then evacuated to a pressure of 10^{-5} mm. of mercury. The electric current was turned on in the heating coil, and the flow of electricity was regulated to a predetermined value. The amount of electricity required

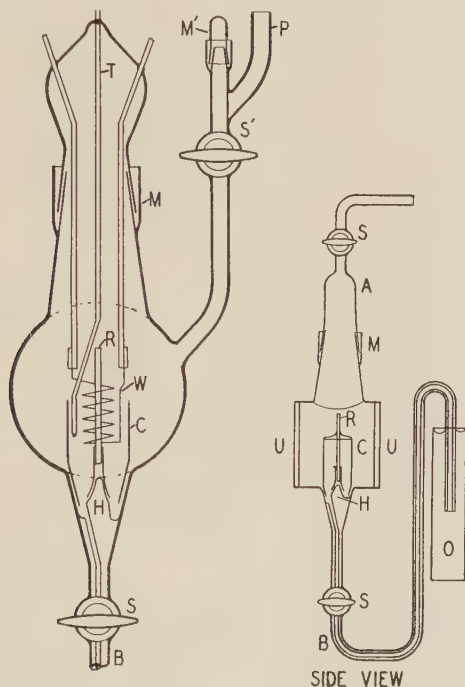


FIG. 2. Main vacuum apparatus

depended upon the temperature of the heat treatment and upon the radiation loss of the apparatus at that temperature. It had to be predetermined for each temperature of heat treatment. The temperature of the metal rods was measured with a calibrated iron-constantan thermocouple, T, in conjunction with a potentiometer and galvanometer. For the pre-treatment to give a standard reference surface, this temperature was 100°C .

The time-temperature curve for the approach from 25°C . to the desired temperature of treatment was plotted so that the exact amount of heat energy communicated to the metal could be duplicated in subsequent measurements. When the temperature had attained the constant value of

100°C. (or whatever temperature was being used), the system was allowed to remain thus for exactly one hour, after which the current was turned off and the entire apparatus allowed to cool, the vacuum being carefully replaced with pure nitrogen. The time rate of cooling from a given temperature was made the same for each rod.

A blank run was made before each measurement at the temperature to be used in the measurement proper. This run was made in the hope of eliminating gases dissolved in the glass of the apparatus, which might be given off at the higher temperatures. In this way, it would seem that any gases given off from the glass up to and at the given temperature would be eliminated and pure nitrogen resorbed in their place. In the subsequent measurement at the same temperature, less, or practically no, foreign gases should be evolved from the glass. Nitrogen was kept flowing through the cooled apparatus until it was ready for the measurement proper.

A liquid-air trap was used between the apparatus and the vacuum pump. The vacuum pump was a mercury-vapor pump backed by a high-vacuum oil pump, used in conjunction with a McLeod gauge. All joints and stop-cocks were of the mercury-seal type.

After a rod had been polished and heat treated at 100°C. to bring its surface to the standard reference condition, its surface condition was determined by measurement of the metal-water-nitrogen contact angle. This measurement was carried out in the following manner:

When the rod had cooled to 25°C., the heating unit was removed, with nitrogen flowing through the apparatus, and the unit A (figure 2, side view) attached in its place. The nitrogen line was disconnected, and the siphon attached in its place by means of the ground-glass joint. Water was then siphoned into the glass cup or cell, C, in the apparatus. The advancing contact angle was thus formed. Several measurements could be made on the same rod by raising the siphon reservoir and causing the liquid to advance slightly before each measurement. Lowering the siphon reservoir gave the receding angle. Each angle was either photographed or projected directly onto a special screen for measurement, as described in a previous communication (2). These angles could be readily duplicated to $\pm 2^\circ$. A minimum of three check runs was made on each system investigated. The tabulated results represent the averages of all runs for a given system.

MANIPULATION OF VACUUM APPARATUS FOR THE MEASUREMENT OF SOLID-LIQUID-LIQUID CONTACT ANGLES

For the measurement of solid-liquid-liquid interfacial contact angles, various devices, depending upon the relative glass-wetting characteristics and densities of the two liquids, had to be used in conjunction with the apparatus shown in figure 2. The diagrammatic sketches of such mechan-

ical devices have appeared in a previous paper (2). Except for the use of these additional devices the manipulation of the apparatus was the same as for the measurement of solid-liquid-gas contact angles.

TABLE 1

Alteration of magnitude of contact angles of several metals upon heat treatment of the metals in vacuum

HEATED 1 HOUR IN A VACUUM AT °C	METAL-H ₂ O-N ₂			METAL-H ₂ O-C ₆ H ₆			METAL-H ₂ O-AcBr ₄			METAL-H ₂ O-α-BrN		
	θ ₁₃	K ₁₃	A ₁₃	θ _{n3}	K _{n3}	A _{1n}	θ _{n3}	K _{n3}	A _{1n}	θ _{n3}	K _{n3}	A _{1n}
Gold												
100	72°	0.309	22.3	180°		(139.3)	180°		(149.0)	180°		(163.5)
200	35°	0.819	59.0	120°	-0.500	76.3	120°	-0.500	78.1	120°	-0.500	79.8
Platinum												
100	65°	0.423	30.4	180°		(125.1)	180°		(133.5)	180°		(145.5)
200	32°	0.848	61.1	108°	-0.309	71.8	109°	-0.326	73.5	109°	-0.326	74.6
Copper												
100	60°	0.500	36.0	180°		(115.5)	180°		(122.8)	180°		(132.0)
150	40°	0.766	55.2	139°	-0.755	81.3	140°	-0.766	84.5	140°	-0.766	88.8
200	28°	0.883	63.6	96°	-0.105	67.2	96°	-0.105	67.6	96°	-0.105	67.9
250	20°	0.940	67.7	80°	0.191	61.0	80°	0.191	60.4	80°	0.191	59.7
18-8 stainless steel												
100	41°	0.755	54.3	144°	-0.809	82.4	146°	-0.829	86.1	144°	-0.809	88.0
150	10°	0.990	70.9	64°	0.438	55.7	64°	0.438	54.1	64°	0.438	52.7
200	0°		(75.3)	40°	0.766	48.6	38°	0.788	45.1	38°	0.788	42.6
250	0°		(76.2)	32°	0.848	46.8	30°	0.866	43.7	31°	0.857	40.9

* The symbols used in this paper are the same as those used in recent papers from this laboratory, i.e., S represents surface tension, interfacial tension, or free surface energy, A represents adhesion tension, θ the contact angle, and K is the same as the cosine of θ within the limits of +1 and -1, but may take on values greater than +1 and less than -1. The subscripts 1, n , and 3 refer to the solid, any organic liquid, and water, respectively. AcBr₄ = acetylene tetrabromide; α-BrN = α-bromonaphthalene. Values in parentheses were extrapolated from diagram.

ALTERATION OF MAGNITUDE OF CONTACT ANGLES OF METALS ON HEAT TREATMENT OF THE METALS IN A VACUUM

The results of the investigation of contact angle changes on heat treatment of metals in a vacuum are given in table 1. All the angles given in

table 1 are "equilibrium" advancing angles. The metal-water-nitrogen angle for a given metal heat-treated in a vacuum decreased in a regular manner with increasing temperature of heat treatment. For a given temperature of heat treatment the magnitude of this angle for the different metals varied in the order of their apparent reactivity. This might seem to indicate oxide film formation, due to the presence of traces of oxygen during the heating process, since progressive oxide film formation would give increasingly hydrophilic surfaces and decreasing contact angles with water. No temper colors, i.e., no visible indications of an oxide film, were noted, however, on any of the metals, even when they were treated for

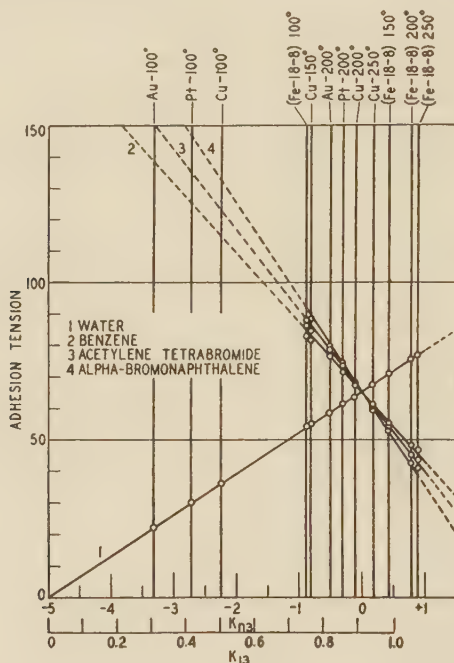


FIG. 3. K_{n3} versus adhesion tension

long periods of time at over 400°C. in the vacuum apparatus. It seems more probable, therefore, that heat oxidation had been eliminated in the vacuum apparatus, and that the decrease in the contact angle was caused by changes in the crystal structure of the metal during the heat treatment. Sorption of nitrogen by the metals probably also took place.

For the three different liquid-liquid systems tested, the interfacial contact angles on a given metal, heat-treated at a given temperature in a vacuum, were all the same within the limits of experimental error. The empirical equations of Bartell and Bartell (1) may then apply to these metals heat-treated in a vacuum. When the data obtained are plotted on

a K_{n3} versus adhesion tension graph, as shown in figure 3, the points lie in straight lines whose equations are the equations cited above.

The progressive alteration of the contact angles of metals heat-treated in a vacuum is in accordance with results previously obtained for heat treatment of metals in air (3), and lends assurance to the previous conclusion that crystallization phenomena are in part responsible for such changes.

METHOD OF HEAT TREATMENT OF METALS IN DIFFERENT GASES

Standard surface rods were polished in the given gas in the apparatus shown in figure 1, transferred in an atmosphere of that gas to an especially designed induction furnace, and heated for one hour at 200°C. in the same gas at atmospheric pressure. The furnace was so designed that the rod could be loaded into it from the transferring unit, L, of the polishing apparatus, without coming into contact with air. The rod was freely suspended in the interior of the furnace without more than 2 mm. contact with any solid, i.e., the glass of the furnace interior. The current of gas entered from the rear to facilitate loading without introduction of foreign gases. After heating, the rods were removed by a special holder into a cooling compartment through which the given gas was flowing, and after rapid cooling to 25°C., transferred to the main apparatus, figure 2, which had previously been flushed out with the same gas. The measurements of contact angles were made in an atmosphere of this gas at atmospheric pressure. With surfaces treated in this manner, the contact angle could be checked in the majority of cases to $\pm 4^\circ$.

ALTERATION OF MAGNITUDE OF CONTACT ANGLES OF METALS HEAT-TREATED IN DIFFERENT GASES

Some of the results obtained with metals heated in nitrogen and in hydrogen are given in table 2. For these metal-water-nitrogen and metal-water-hydrogen systems the angles formed showed no tendency to change over relatively long periods of time and were, apparently, equilibrium angles.

Table 3 gives the initial metal-organic liquid-nitrogen and the metal-organic liquid-hydrogen advancing contact angles for metals heated in nitrogen and in hydrogen, respectively. These initial angles are contact angles obtained immediately after immersion of the cooled metal rod into the organic liquid. They are finite, reproducible, advancing contact angles, but they decrease to zero angles with time. Somewhat analogous effects were obtained with rods which had been heated in oxygen.

Heating the metal rods in hydrogen or nitrogen apparently caused such a profound change in the surface structure (and, hence, in the free surface energy) that chemical reaction took place between the metal and the halogenated organic liquids used in this investigation. When such

TABLE 2

Contact angles of water on several metals and alloys heat-treated in various gases at 200°C. for one hour

METAL	METALS HEATED IN NITROGEN			METALS HEATED IN HYDROGEN		
	Metal-water-nitrogen angles			Metal-water-hydrogen angles		
	θ_{12}	K_{12}	A_{12}	θ_{12}	K_{12}	A_{12}
Gold.....	80°	0.174	12.5	56°	0.559	40.3
Platinum.....	58°	0.530	38.2	42°	0.743	53.3
Silver.....	69°	0.358	25.8	48°	0.669	48.2
Copper.....	90°	0.000	0.0	66°	0.407	29.3
Steel (18-8).....	78°	0.208	15.0	60°	0.500	36.0
Aluminum.....	74°	0.276	19.8	70°	0.342	24.6
Tungsten.....	40°	0.766	55.2	68°	0.375	27.0
Brass.....	110°	-0.342	-24.6	43°	0.731	52.7

TABLE 3

Initial contact angles of organic liquids on several metals and alloys heat-treated in various gases at 200°C. for one hour

METAL	HEATED IN NITROGEN ATMOSPHERE						HEATED IN HYDROGEN ATMOSPHERE		
	Metal-acetylene tetra-bromide-nitrogen			Metal- α -bromonaphthalene-nitrogen			Metal-acetylene tetra-bromide-hydrogen		
	θ_{1n}	K_{1n}	A_{1n}	θ_{1n}	K_{1n}	A_{1n}	θ_{1n}	K_{1n}	A_{1n}
Gold.....	30°	0.866	42.4	8°	0.990	44.6	0°		
Platinum.....	0°			0°			0°		
Silver.....	12°	0.978	47.9	0°			0°		
Copper.....	34°	0.829	40.6	12°	0.978	43.0	0°		
Steel (18-8).....	26°	0.899	44.0	0°			0°		
Aluminum.....	22°	0.927	45.4	0°			25°	0.906	44.5
Tungsten.....	0°			0°			20°	0.940	46.2
Brass.....	45°	0.707	34.6	16°	0.961	42.3	0°		

TABLE 4

Comparison of contact angles of water on gold and on platinum heat-treated one hour at 200°C. in a vacuum and in several gases

HEATED IN	GOLD			PLATINUM		
	θ_{12}	K_{12}	A_{12}	θ_{12}	K_{12}	A_{12}
Vacuum.....	35°	0.819	59.0	32°	0.848	61.1
Hydrogen.....	56°	0.559	40.3	42°	0.743	53.3
Air.....	57°	0.5446	39.21	49°	0.6561	47.24
Nitrogen.....	80°	0.174	12.5	58°	0.559	38.2

heat-treated rods were immersed in α -bromonaphthalene or in acetylene tetrabromide which had previously been saturated with water, metallic bromides were formed with those metals which exhibited finite initial contact angles. Metallic bromides were not formed with metals whose initial contact angle was zero.

Though one is not justified in calculating adhesion tension for a system which is not in equilibrium, adhesion tension values calculated from the initial advancing metal-organic liquid contact angles given in table 3 are some linear function of the adhesion tension of the corresponding metal-water-air contact angles (table 2). It is impossible, at present, to assign a precise meaning to such relations.

In table 4 the effects of heating gold and platinum in a vacuum and in several gases are compared through comparison of the metal-water-gas contact angles and the corresponding adhesion tensions. Gold and platinum are made progressively less hydrophilic by heat treatment in a vacuum, in hydrogen, in air, and in nitrogen, in the order given. For those solids to which the Bartell-Bartell (1) equations apply, a decrease in hydrophilic properties indicates a corresponding increase in organophilic properties. That these heat-treated metals have been made progressively organophilic is indicated by the fact that the least hydrophilic of them, the gold heated in nitrogen, actually reacted with α -bromonaphthalene and with acetylene tetrabromide.

SUMMARY

1. Rods of gold, platinum, copper, 18-8 stainless steel, silver, aluminum, tungsten, and brass were pretreated so as to have standard reference surfaces.

2. Heat treatment of the metals in a vacuum caused them to become more hydrophilic with increasing temperature of heat treatment.

3. The metals became progressively less hydrophilic when heat treated in a vacuum, in hydrogen, in air, and in nitrogen, in the order stated.

4. All the metals except platinum and tungsten, when heat treated in nitrogen, readily reacted chemically with acetylene tetrabromide; gold, copper, and brass, similarly heat treated, reacted with α -bromonaphthalene. Aluminum and tungsten, heat treated in hydrogen, reacted with acetylene tetrabromide.

5. The wetting characteristics of the different metals differ greatly, and the wetting characteristics of surfaces of the same metal differ greatly, depending upon the precise pretreatment of the metal.

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